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Department of Physics

Queen's University
Kingston, Canada

THE DEVELOPMENT OF CERAMIC PROTON CONDUCTORS

FINAL REPORT

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M.F. Bell and M. Sayer
Department of Physics
Queen's University
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on behalf of the Energy, Mines and Resources, Canada.

Canada Centre for Mineral and Energy Technology

Scientific Authority: Dr. T.A. Wheat

In recent years, there has been a continuing interest in the development of ionically conducting solids. In particular, the search for hydrogen ion conductors has intensified due to their potential application in a large number of devices including fuel cells and water electrolysis units. This latter application has been demonstrated with a solid polymer electrolyte developed by General Electric (1). This material is a plastic sheet of perfluorinated sulphonic acid polymer and has a conductivity of $6 \times 10^{-2} \Omega^{-1} cm^{-1}$ when saturated with water. However, although it has many advantages, it is expensive to produce (450$ per m^2) which may restrict it s application. This has led to the search for less expensive, inorganic hydrogen conductors especially compounds which are stable at 200 - 300°C. The research in this area is reviewed in the first section of this report. The second section discusses the experimental data on proton conductors collected under this contract.

SECTION 1 Recent Developments in Hydrogen Ion Conductors

Research on proton coduction up to 1973 has been reviewed by Glasser (2) and updated by Sayer (3) who was principally concerned with the β alumina system. Later

work has been discussed by Nicholson (4). It is the purpose of this report to review the more recent work in the field of inorganic hydrogen ion conductors indicating their conductivity and stability range. As the mechanism for proton motion will have important consequences in terms of the conductivity and stability, this will also be discussed.

1.1 Conductivity Mechanism

Various mechanisms for proton diffusion may be considered. They include the Grotthus mechanism involving proton exchange between H_2O and H_3O^+, complex ion diffusion and single particle migration (i.e. single proton jumps or tunnelling). A mechanism involving single particle migration would be expected to take place in largely dehydrated compounds and would tend to lead to low conductivity. Thus this mechanism has been proposed for proton diffusion in the defect pyrochlore $HTaWO_5$ (5) on the basis of NMR data. The conductivity of this compound has not been measured although the NMR data suggests a maximum value of $10^{-6}\Omega^{-1}cm^{-1}$ at room temperature. In contrast, the Grotthus mechanism requires a relatively close proximity of water molecules which must be held firmly but have the ability to rotate. However it is usually found that compounds that have a high enough water concentration to

support a Grotthus mechanism readily dehydrate at low temperatures with a concomitant decrease in conductivity. It is more likely therefore that compounds which are stable at higher temperatures and exhibit high conductivity will conduct via the complex ion or 'vehicle' mechanism. This mechanism involves the diffusion of a nucleophilic group such as the hydronium ion in which the water molecule acts as a carrier or vehicle for the proton. For this mechanism to operate, the proton shoud be only weakly held to the anionic lattice and thus the Bronsted acidity will be an important property for a good proton conductor. For example, for acids of the type H_xMO_y, the acid strength tends to increase as one proceeds up a group or to the right within a row of the periodic table. This occurs because the proton is less strongly held as the MO bond becomes stronger. Obviously the ability of the carrier to act as a base is also important and other carriers such as NH_3 have been shown to increase the conductivity in some instances.

From the discussion above, it can be seen that it is unlikely that a single mechanism will explain all cases. In fact, within a single compound there may be a competition between these mechanisms depending on the carrier concentration. At high concentrations, the Grotthus mechanism is expected to dominate. However, as

dehydration occurs, there becomes more room (sites) for the carrier molecule to be mobile and vehicle transport will become more important. At very low carrier concentrations, proton motion will occur via proton tunnelling and the conductivity is expected to be low.

1.2 Examples

In many instances, the ease of ion exchange has been taken as a first indication of high ionic conductivity and this has led to the investigation of compounds which exhibit good ion exchange properties. Ion exchangers can be classified into the following groups:

1) Heteropolyacids (e.g. $H_3Mo_{12}PO_{40}.29H_2O$)
2) Acid phosphates ($Zr(HPO_4)_4.4H_2O$)
3) Hydrous oxides ($H_2Sb_4O_{11}.nH_2O$)
4) Aluminosilicates (zeolites and clays)

The following examples are used to illustrate the consequences of mechanism on the conductivity and thermal stability of compounds in each of these groups. A separate section will discuss recent work on the β alumina system which also shows good ion exchange properties and is probably the most widely studied fast proton conductor.

1.2.1 Heteropolyacids

The best protonically conducting solids reported to date are the heteropolyacids, $H_3Mo_{12}PO_{40}.29H_2O$ (PMA) and $H_3W_{12}PO_{40}.29H_2O$ (PWA) whose room temperature conductivity is 0.2 $\Omega^{-1}cm^{-1}$(6). Even the lower hydrates which exist at lower vapour pressures have been shown to have conductivities of the order of $10^{-2}\Omega^{-1}cm^{-1}$(6). Some doubt arises concerning their stability however. Nakamura et al(7) studied the phase diagram up to 70°C and found a number of stable hydrates depending on the temperature and water vapour pressure. However Childs et al (8) reported that these compounds melt at 40°C. As expected, these salts are very soluble and tend to be easily reduced by hydrogen. Moreover they are very corrosive to metals (8) and may not therefore find commercial application.

1.2.2 Acid phosphates

Protonic conduction has been known to occur in the acid phosphates for over twenty years (9). The layered compound, $Zr(HPO_4)_4.4H_2O$, was found to have a room temperature conductivity of $5 \times 10^{-5}\Omega^{-1}cm^{-1}$ with an activation energy of 0.26 eV (9). However the material has a tendency to gel formation and higher conductivities have been reported (10,11) probably due to surface conduction. In the crystalline state, the material is difficult to

press and suffers from water loss at low vapour pressures. Moreover it releases phosphoric acid on reaction with water (12). Better properties (up to 150°C) are obtained using admixtures with zeolites which can then be sintered into strong discs (13).

Fast proton conduction has also been reported in another acid phosphate, hydrogen uranyl phosphate (HUP) (14-16). HUP belongs to a class of compounds whose general formula may be written as $M^{M+}_{1/M}(UO_2XO_4).nH_2O$ where M represents a mono- or di-valent cation and X may be P, As, V or mixtures of these. HUP has a room temperature conductivity of $4 \times 10^{-3} \Omega^{-1}cm^{-1}$ (14) making it one of the better protonic conductors reported to date. However it dehydrates as low as 30°C depending on the water vapour pressure (15). The initial dehydration product (3 molecules of water) has a hundred fold lower conductivity (15). The decomposition voltage ($\sim$2V) is high enough to permit operation of electrochemical cells (17) but this compound may be reduced by hydrogen (12). The arsenate analogue has been shown to have a high conductivity but the compound suffers from the same problems as HUP. Replacing the phosphate by periodate also produces compounds which exhibit high conductivity but this system is ill defined at present (15,16).

1.2.3 Hydrous oxides/hydroxides (hydrates)

A number of papers have appeared recently dealing with proton transport in hydrates. Two classes of hydrates have been distinguished. The particle hydrates consist of small oxide particles in which a satisfactory surface-metal coordination is achieved by the addition of surface water. Additional water molecules occupy the interparticle spaces to produce a connected 'viscous-liquid' region through the composite solid. Proton transport may not occur through the solid particles but it does occur through the aqueous interparticle region. In contrast, external surface structure and surface equilibrium become less dominant in the framework hydrates and high conductivity nescessitates transport through, rather than around, each particle. Interestingly, a wide range of conductivities have been measured on these materials (Table 1). However their thermal stability is very low. Although the preparation of dense ceramics of the particle hydrates by cold-pressing is a clear advantage, other problems associated with their solubility and stability towards reduction by hydrogen limit the possibility of their potential application.

Aluminosilicates

The zeolites are a class of aluminosilicate compounds which exhibit a wide range of network structures

and are widely known for their ion exchange properties. As discussed previously, the extent of association of the H^+ ions with the basic sites on the channel walls is expected to influence the conductivity. In anhydrous material, it is generally accepted that the protons are attached to the framework in the form of OH groups and there is evidence of only low conductivity. Thus, at elevated temperatures where the zeolites are essentially anhydrous, NMR studies (25) indicate a maximum conductivity of $10^{-7}\Omega^{-1}cm^{-1}$ at 200°C for selected zeolites. Recently, however, Johnson et al (26) reported high conductivities ($10^{-4}-10^{-5}\Omega^{-1}cm^{-1}$ at 25°C) for the 'fully' hydrated hydronium analogues of mordenite and natrolite. The latter compound was studied for improved thermal stability as, in contrast to other zeolites which generally suffer from continuous dehydration above ambient temperature, the narrow channel structure of the natrolite class allows the retention of the water of hydration up to approximately 200°C. However, as later recognised by these authors (27), this narrow channel structure should preclude high conductivity and, after drying at 30°C, a conductivity of $10^{-10}\Omega^{-1}cm^{-1}$ was measured thus implicating surface conduction in the earlier measurements. Similar results were obtained for the mordenite compound.

According to the vehicle mechanism, the use of a

stronger base such as ammonia should reduce the extent of association of the proton with the framework (28,29). This conclusion led to a wide range of ammonium zeolites (Tables 2 and 3) which are the subject of a german patent (30). The highest conductivity ($2 \times 10^{-3} \Omega^{-1} cm^{-1}$) was obtained for the ammonium analogue of zeolite A (29). This conductivity is 4 orders of magnitude higher than the hydronium ion form (Table 3). It was inferred from infrared data that this was due to the formation of the ammonium ion whereas water is not a strong enough base to disassociate the proton from the framework. Interestingly methylammine could also be used as a carrier for the proton and a conductivity of $7 \times 10^{-5} \Omega^{-1} cm^{-1}$ was measured at room temperature (Table 3). As expected this is lower than that of the ammonium derivative but indicates the validity of the vehicle mechanism in this system. The role of hydration in these compounds is unclear although it may be possible that the water molecules are necessary to reduce basicity of the framework by hydrogen bonding. The incorporation of alcohols produces similar effects (Table 3). As the ammonia and water molecules are held by only weak interactions, the thermal stability of these compounds is low. They dehydrate at around 30°C and suffer NH_3 loss at 80°C. In the study of proton conduction in natrolite and mordenite discussed previously, Lal et al (27) measured the

conductivities of the ammonium analogues. In the case of natrolite, the channel structure is too narrow to allow rapid motion of the ammonium ions and the influence of surface water was again evident, the conductivity decreasing from $10^{-4}\Omega^{-1}cm^{-1}$ for a wet sample to less than $10^{-10}\Omega^{-1}cm^{-1}$ in the 'dry' state. However the ammonium analogue of mordenite showed only a decade decrease in conductivity on drying the sample. This compound may be a hydrogen ion conductor with a room temperature conductivity of $10^{-5}\Omega^{-1}cm^{-1}$. No information is available on the thermal stability of this compound but it is expected to be low.

H-montmorillite clay is another class of aluminosilicate which exhibits high proton conductivity ($4 \times 10^{-3}\Omega^{-1}cm^{-1}$) at room temperature (31). This compound has a layer structure and it is believed that the interlayer water is 'liquid-like', thus permitting a high conductivity. The conductivity is dependent on the amount of exchanged iron and aluminium and also on the extent of hydration.

1.2.5 Protonic β aluminas

β alumina is a general term for two phases (β and β'') with closely related structures. A variety of cations including Na^+, K^+ and Ag^+ as well as H_3O^+ and NH_4^+ can be incorporated into the structure. It is generally

found that the structural differences tend to allow higher conductivity in β'' alumina than in the β phase. In the case of the hydronium analogues, a large difference (several orders of magnitude) in conductivity was reported (32) which could not be explained on the small structural differences. However later reports by the same authors (33,34) suggest that the originally, anomalously high conductivity of the β'' phase was primarily associated with surface conduction in an adsorbed water layer. These later reports indicate a conductivity of 10^{-5} to $10^{-7}\Omega^{-1}cm^{-1}$ at 25°C. Water loss from the conduction plane occurs between 150 and 300°C leading to a decrease in conductivity (31). However a stable composition exists above these temperatures showing conductivities in the range of 10^{-5} to $10^{-3}\Omega^{-1}cm^{-1}$ between 300 and 400°C (34). Above 400°C, irreversible dehydration occurs.

The increased conductivity of the hydrated ammonium isomorph ($10^{-4}\Omega^{-1}cm^{-1}$ at 25°C (33)) is a possible indication that conduction is via a vehicle mechanism in a similar manner to the aluminosilicates discussed previously. Linear Arrhenius behaviour was observed for this compound up to 200°C when the conductivity decreases as ammonia and water are evolved (33).

1.2.6 Other proton carriers

The structure of lithium hydrazinium sulfate, $LiN_2H_5SO_4$, consists of a framework of SO_4 and LiO_4 tetrahedra forming channels parallel to the c-axis in which the hydrazinium ions ($N_2H_5^+$) are located. As expected, the conductivity is low ($10^{-7}\Omega^{-1}cm^{-1}$) and highly anisotropic (16). Moreover it has a low decomposition voltage ($\sim$35 mV) and is therefore uninteresting for commercial application. However comparison of the measured activation energy (0.7 eV) with calculated values for the rotation and translational movement of the hydrazinium ion suggests that proton motion is via the vehicle mechanism (16). This is therefore an example of a carrier other than water or ammonia taking part in the conduction process. Although water or ammonia would seem better candidates for proton carriers, it may be fruitful to investigate other possibilities.

1.3 Conclusions

The intensive search for proton conductors in recent years has led to the discovery of many compounds with high room temperature conductivity. However all of these compounds have a high water content and readily

dehydrate. Thus, although these compounds may have potential use in room temperature devices, their low thermal stability will restrict application in the thermodynamically more desirable temperature range of 200-300°C. Only two compounds, β alumina and the hydronium analogue of NaZrPSiO, exhibit sufficiently high conductivity and thermal stability to be useful in this temperature range.

SECTION 2 Experimental Measurements

2.1 NaZrPSiO

In this report, the term NaZrPSiO will be used to refer to the solid solution series, $Na_{1+x}Zr_{2-x/3}Si_xP_{3-x}O_{12-3x/3}$ (MP) and $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (H). No separation of these systems will be attempted as the available experimental evidence suggests that they behave similarly. In the NaZrPSiO system, there also exists two phases. The first exhibits monoclinic symmetry and exists at high x values (x>ca. 1.6). In contrast, a rhombohedral phase exists at the phosphorus-rich (x<1.6) end of the series. For convenience, these will be treated separately.

2.1.1 the monoclinic phase.

The conductivity of a NaZrPSiO sample (x=2) obtained from the Max Planck Institute showed a similar temperature dependence (figure 1) to that reported previously (35) although the conductivity was low. Experimental evidence (35) suggests that the change in slope at ca.180°C reflects a phase transition. In contrast, material supplied by CANMET in this phase gave inconsistent and irreproducible results (Table 4). Of the the samples that gave linear Arrhenius behaviour at low temperature, the room temperature conductivity varied over

a large range ($5x10^{-8}$ to $5x10^{-4}$ $\Omega^{-1}cm^{-1}$) in a non-systematic manner. Furthermore a number of samples showed a decrease in conductivity between 200 and 300°C (figure 2). It should be noted that this decrease in conductivity cannot be associated with the phase transition observed on Max Planck material. On temperature cycling, the behaviour was found to be irreproducible and unpredictable (figure 3). During these experiments, it was noted that the electrodes (silver) became discoloured and tended to flake. In extreme cases, the whole sample became black. These observations tend to lead to the conclusion that this material reacts with metallic silver. However it is difficult to understand what this reaction could be or why it occurs on only a few samples.

Further evidence for the high reactivity of this material was obtained from the behaviour in high humidity atmosphere. After only 48 hours in a wet atmosphere (ca. 100% relative humidity), the originally solid, disc-shaped samples had disintegrated into a coarse powder. The X ray powder diffraction pattern (figure 4) showed that decomposition to an unknown compound had occurred. No firm explanation can be given for the high reactivity of this material compared to that prepared at the Max Planck Institute. However recent evidence (36) suggests that this instabilty may be related to the presence of a glassy phase

at the grain boundaries.

2.1.2 the rhombohedral phase.

In this phase, it was found from X-ray powder diffraction studies that the lattice parameter, a, increases linearly with x (figure 5). This increase in cell volume combined with an increase in the concentration(x) of mobile ions produces a non-linear increase in conductivity (figure 6). As shown in figure 6, these results (closed circles) are in agreement with previous measurements (open circles) at the Max Planck Institute. However, samples in this phase (x=1.5) prepared at CANMET again showed irreproducible behaviour (Table 6). As expected, the end component, $NaZr_2P_3O_{12}$, was found to have a very low conductivity (ca. $10^{-10}\ \Omega^{-1}cm^{-1}$ at 25°C). This leads to the conclusion that one sodium ion per molecule is trapped in a site in which it is immobile.

2.2 Ion Exchange and the Proton Analogues of NaZrPSiO.

On immersion of powder samples in acid solution, a rapid increase in pH was observed indicating that exchange proceeds with ease and without degradation in these compounds. However no pH change was observed when the end component, $NaZr_2P_3O_{12}$, was immersed in the acid solution. This again indicates that the sodium ion is

trapped in this molecule and suggest that it may not be possible to fully exchange NaZrPSiO. Infra red measurements on these samples show a broad absorption peak at 3500cm^{-1} both for the starting material and for the exchange product (figure 7). The low intensity peak in the spectrum of NaZrPSiO is consistent with the adsorption of water on the sample surface. A much greater intensity is observed with the exchanged material indicating that water has been incorporated into the lattice. The fact that this band is so broad suggest that the water is mobile within the structure. This is also consistent with the fact that no other bands for species such as $H(H_2O)_n^+$ are observed in this region. However a small peak at 1650 cm^{-1} which appeared in the spectrum of the exchanged product may be associated with the asymmetrical bending mode of H_3O^+ as observed in the case of hydrogen uranyl phosphate and hydrogen uranyl arsenate (15). The exchanged powders showed a NMR spectrum (figure 8) which consisted of a sharp resonance superimposed on a broad one. Although the sharp resonance may be principally due to surface water, the broad one is probably associated with mobile protons in the lattice.

Solid samples were exchanged using the field assisted technique developed in the early part of this contract. In contrast to the parent compounds, the

conductivity of the exchanged compounds in the rhombohedral phase showed no systematic dependence on x (Table 5). Thus some other factor(s) seems to be controlling the conductivity in this phase. This may be related to the extent of exchange and degree of hydration. Further investigations are required to clarify this point.

Below 300°C, samples from the monoclinic phase showed linear Arrhenius behaviour (figure 9) with similar conductivities as measured at the Max Planck Institute. Above 300°C, a decrease in activation energy is observed (figure 9). Similarly heating a sample (x=1.4) to 450°C resulted in a decrease in conductivity (figure 10). These results suggest that dehydration of these compounds occurs at temperatures greater than 300°C. However it should be noted that these measurements were carried out in a 'dry' atmosphere. In a water electrolysis cell, however, the atmosphere would have a 100% relative humidity which would effectively hinder dehydration at the proposed operating temperature.

2.3 Hollandite

Conductivity measurements on Hollandite material supplied by CANMET showed that these materials were insulators at room temperature ($\sigma < 10^{-10}\Omega^{-1}cm^{-1}$). As agreed, therefore, work on these materials was discontinued.

2.4 Conclusions

Ion exchange of NaZrPSiO to produce its proton analogue has been demonstrated. Material with a hydrogen ion conductivity of $10^{-3}\Omega^{-1}cm^{-1}$ at 300°C has been prepared. Other physical methods (IR, NMR) give results which are in agreement with a high hydrogen ion conductivity. Although dehydration seems to occur above 300°C in a 'dry' atmosphere, it is thought that this will not be a major problem under the proposed operating conditions.

SECTION 3 CONCLUSIONS AND RECOMMENDATIONS

From a review of the literature, there seems to be a number of compounds which exhibit a high hydrogen ion conductivity at room temperature. However these materials suffer from low chemical and thermal stability. At the thermodynamically more desirable operating temperature of 200-300°C, only β alumina and the hydronium analogue of NaZrPSiO show sufficiently high conductity and thermal stability. However there is much discussion in the literature concerning the composition, structure and chemical stability of NaZrPSiO. It is felt therefore that a deeper understanding of this complex system must be gained before the proton conducting properties can be sensibly studied. Future work should be concerned with this problem.

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Table 1

Conductivity Data for Some Hydrates

Oxide	Water of Hydration	Conductivity (Ω^{-1} cm^{-1})	Activation Energy (eV)	Reference
Sb_2O_5	6.26	2.8×10^{-3}	0.14	20
	5.43	7.5×10^{-3}	0.10	20
	5.36	1.7×10^{-3}	0.10	20
	3.0	2.0×10^{-3}	0.67	19
	1.5	2.0×10^{-6}	0.69	19
ThO_2	4.6	4.0×10^{-4}	0.13	20
	4.2	2.5×10^{-4}	-	20
	3.4	4.0×10^{-5}	-	20
	2.9	5.0×10^{-6}	-	20
$In(OH)_3$	1.42	3.5×10^{-3}	0.15	20
	1.35	1.6×10^{-3}	0.16	20
	1.28	1.2×10^{-3}	0.15	20
$Cr(OH)_3$	2.7	10^{-5}	0.10	20
$Al(OH)_3$	1	6.0×10^{-8}	0.23	20
ZrO_2	(variable)	10^{-4} - 10^{-5}		
SnO_2	2	4.1×10^{-4}	0.15	12

Table 2

Room Temperature Conductivities and Water Content of Fully Hydrated Ammonium Zeolites (from 29)

Zeolite	Conductivity (25°C) (Ω^{-1} cm^{-1})	Water Content (wt %)
analcine	2×10^{-4}	6.5
gismondine	8×10^{-5}	16.0
sodalite	2×10^{-4}	24.5
zeolite A	2×10^{-3}	14.5

Table 3

Room Temperature Conductivity of Derivatives of Zeolite A (from 29)

Derivative	Conductivity (25°C) (Ω^{-1} cm^{-1})
NH_4Zeolite A. nH_2O	2×10^{-3}
CH_3NH_3 Zeolite A. nH_2O	7×10^{-5}
NH_4 Zeolite A. nCH_3OH	1.3×10^{-4}
NH_4 Zeolite A. nC_2H_5OH	1.5×10^{-4}
H Zeolite A. nH_2O	6×10^{-7}
Na Zeolite A. nH_2O	5×10^{-7}

TABLE 4: CONDUCTIVITY DATA FOR MATERIAL PREPARED AT CANMET

x	σ_{RT} ($\Omega^{-1}cm^{-1}$)	σ_{300} ($\Omega^{-1}cm^{-1}$)	Ea eV	Canmet Code
1.8 (1)[a]	4.8×10^{-4}	8.5×10^{-2}	0.315	M20-Na-1225-1
(2)	1.5×10^{-4}	3×10^{-2}	0.322	J33
(3)[a]	3.6×10^{-5}	3×10^{-2}	0.394	J34
1.9[ab]	2.4×10^{-4}	1.2×10^{-1}	0.37	M20-Na-1225-1
2.1[b]	4.6×10^{-7}	6.6×10^{-4}	0.43	M20-Na-1325-15
2.2[b]	1.8×10^{-6}	9.2×10^{-4}	0.37	M20-Na-1350-15
2.3 (1)[ab]	2.9×10^{-5}	1×10^{-2}	0.35	M20-Na-1390-1
(2)[ab]	- no linear portion -			M20-Na-1390-15
2.4 (1)[b]	5.5×10^{-4}	1.2×10^{-1}	0.325	M20-Na-1350-15
(2)[ab]	2.6×10^{-4}	1.4×10^{-2}	0.25	M20-Na-1350-30
3.0 (1)[a]	4.0×10^{-7}	1.1×10^{-3}	0.46	Aug. 17/81 #2 sintered 1200-30 min
(2)	2.0×10^{-8}	8.7×10^{-4}	0.61	Aug. 17/81 #3 sintered 1050-60 min

a non-linear behaviour.

b NASICON formula.

TABLE 5 : CHARACTERIZATION OF THE RHOMBOHEDRAL PHASES OF NAZRPSiO AND HAZRPSiO

x	NAZRPSiO			HAZRPSiO		
	σ_{RT} ($10^{6}\Omega^{-1}cm^{-1}$)	σ_{300} ($10^{3}\Omega^{-1}cm^{-1}$)	E (eV)	σ_{RT} ($10^{8}\Omega^{-1}cm^{-1}$)	σ_{300} ($10^{-4}\Omega^{-1}cm^{-1}$)	E (eV)
0.3	8.0	8.0	0.40	17	10.0	0.50
0.5	2.0	1.6	0.39	4.9	0.9	0.44
0.8	7.0	8.6	0.42	12	9.0	0.52
1.0	27	19	0.39	16	9.6	0.50
1.4	46	27	0.38	30	5.0	0.44
1.5	150	94	0.38	17	11.0	0.50
1.5	110	16	0.30	-	-	-

TABLE 6 CONDUCTIVITY DATA FOR MATERIAL IN THE RHOMBOHEDRAL PHASE PREPARED AT CANMET

NaZrPSiO x = 1.5

sintering temp. C	sintering time hr	density g/cm^3	conductivity T = 25°C $10^4\Omega^{-1}cm^{-1}$	conductivity T = 300°C $10^2\Omega^{-1}cm^{-1}$	activation energy eV	linear region °C	CANMET CODE
1150	1	3.10	1.1	1.7	0.31	280	#6 MP
1150	16	3.07	1.2	10.0	0.40	210	#8 MP
1150	1	3.06	0.4	2.1	0.37	220	#13MP
1150	16	3.06	0.38	8.7	0.45	181	#21MP
1300	1	3.21	8.3	34	0.36	185	#7 H
1300	16	3.16	6.2	3.1	0.25	220	#11H

figure 1 Conductivity of NaZrPSiO (x=2) as a function of inverse temperature.

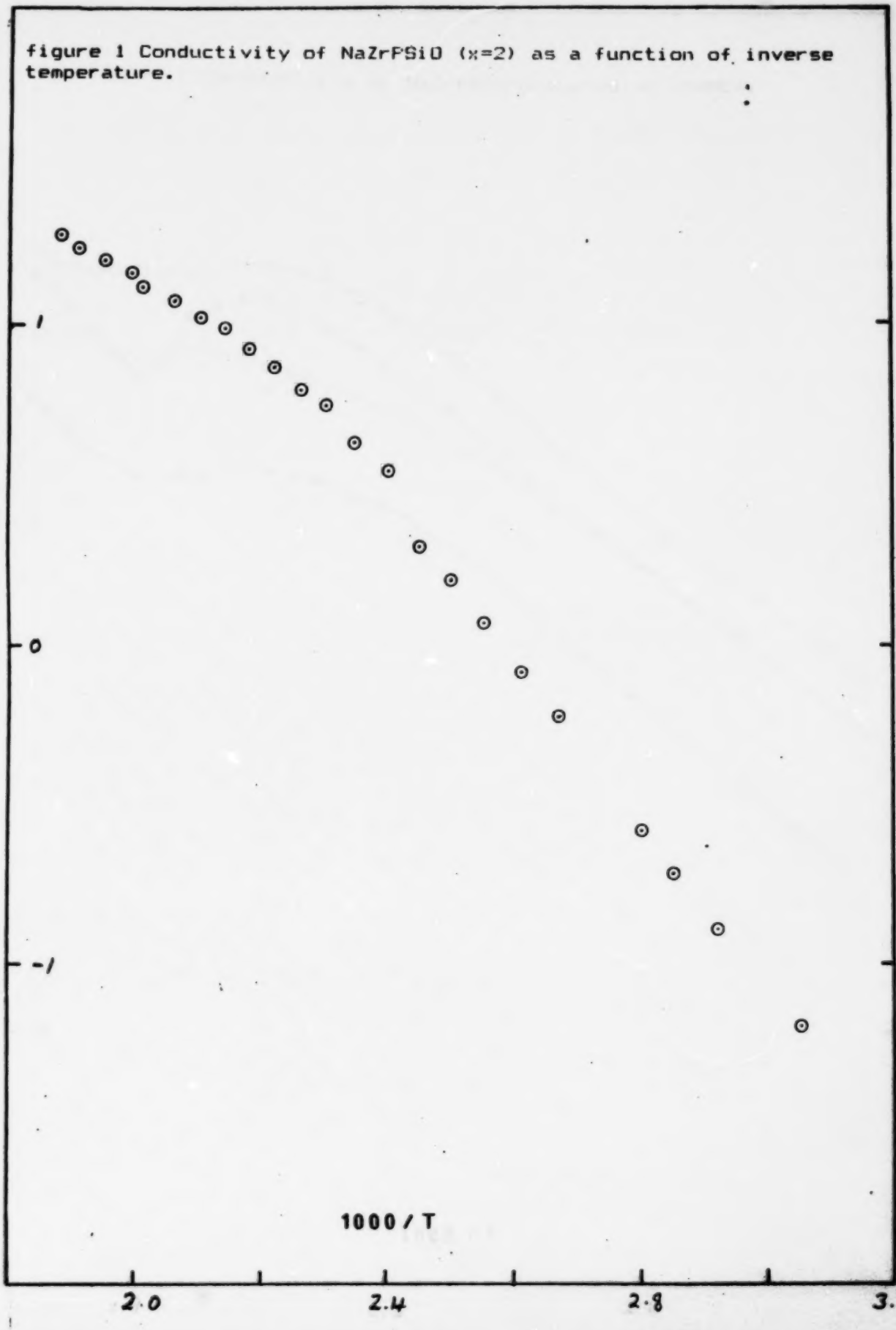


Figure 2 Conductivity of NaZrPSiO prepared at CANMET.

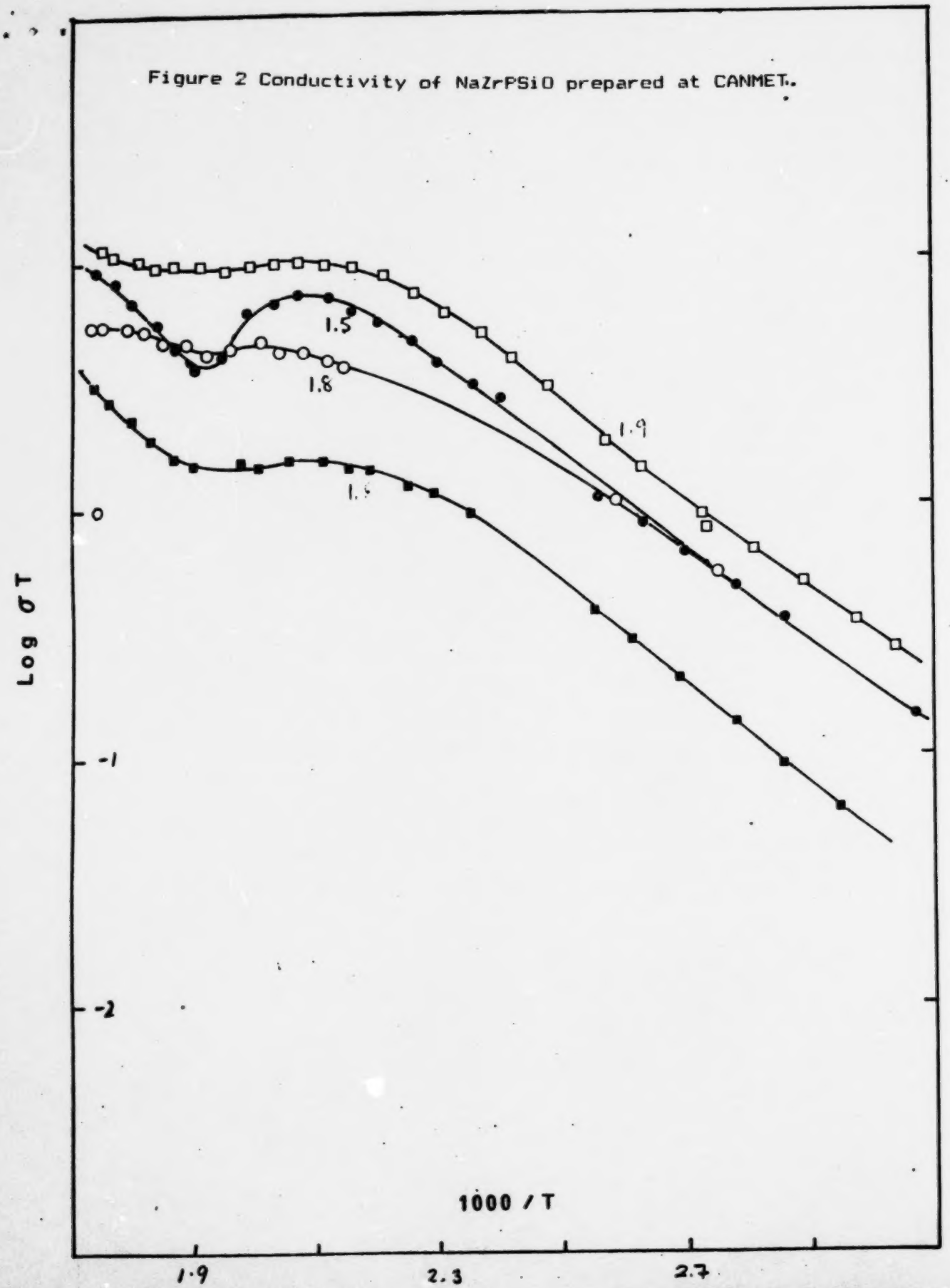
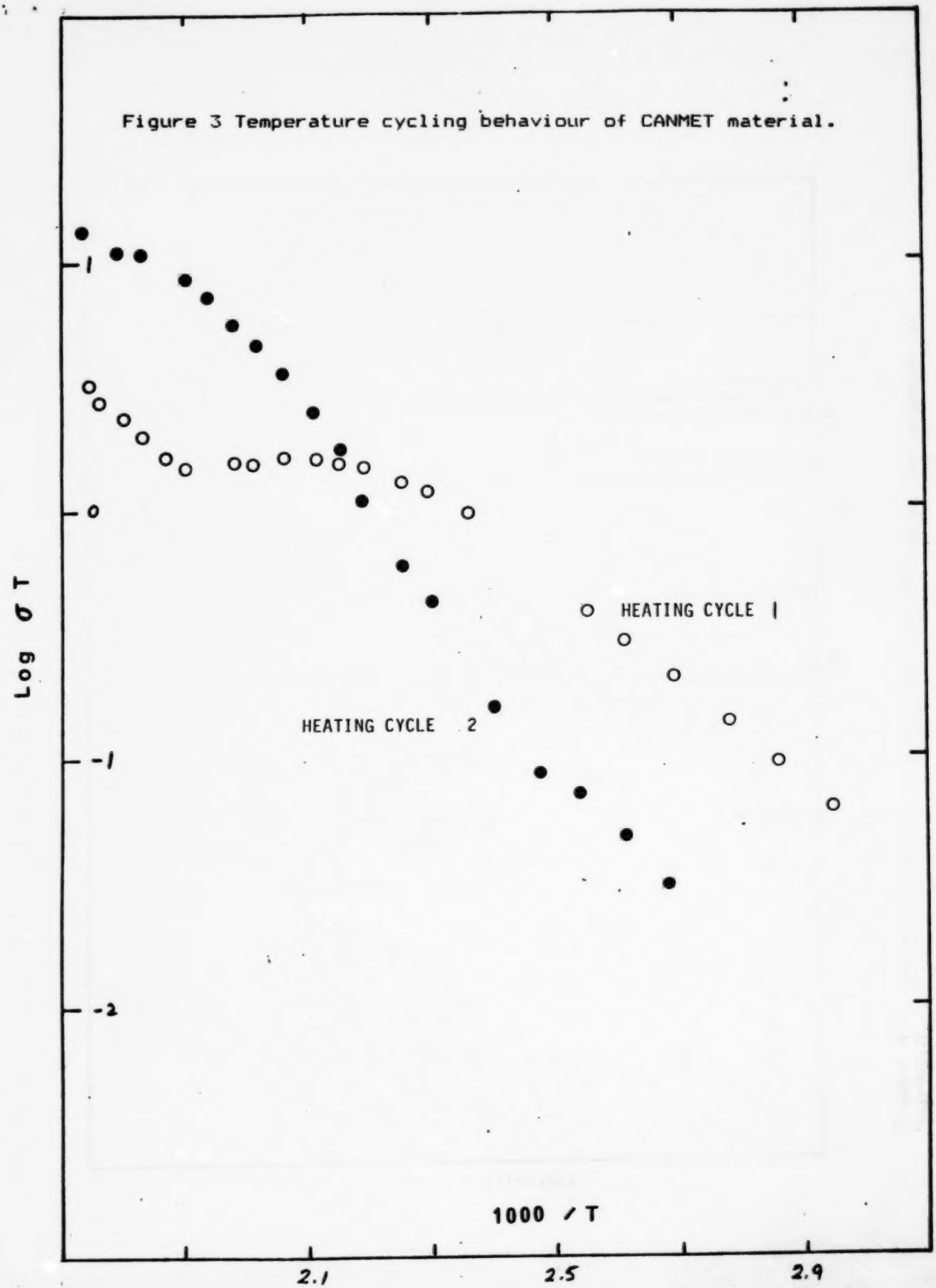


Figure 3 Temperature cycling behaviour of CANMET material.



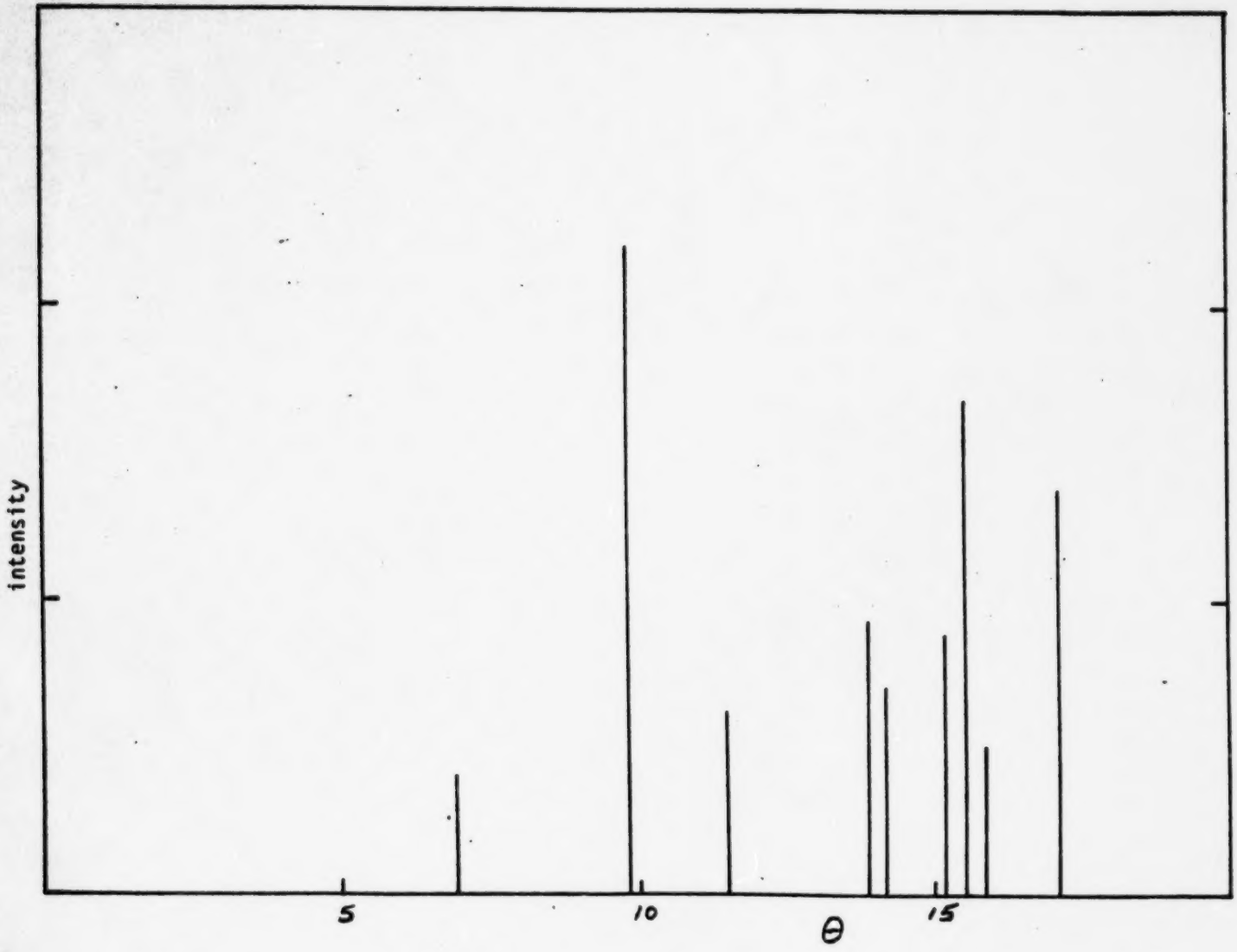


Figure 4 X ray diffraction pattern for the decompositon product of NaZrPSiO.

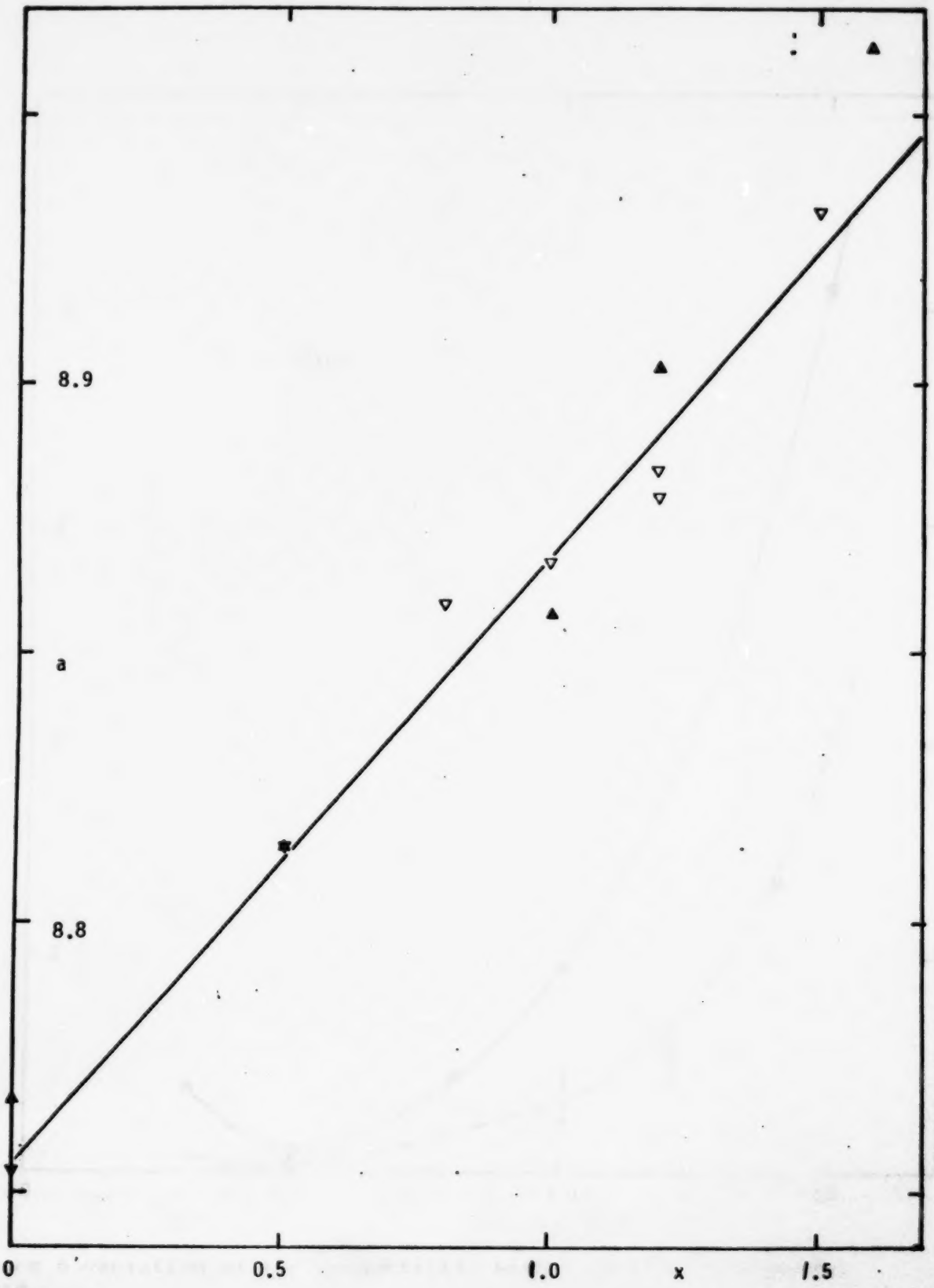


Figure 5 Variation of the lattice parameter, a, with x in the rhombohedral phase.

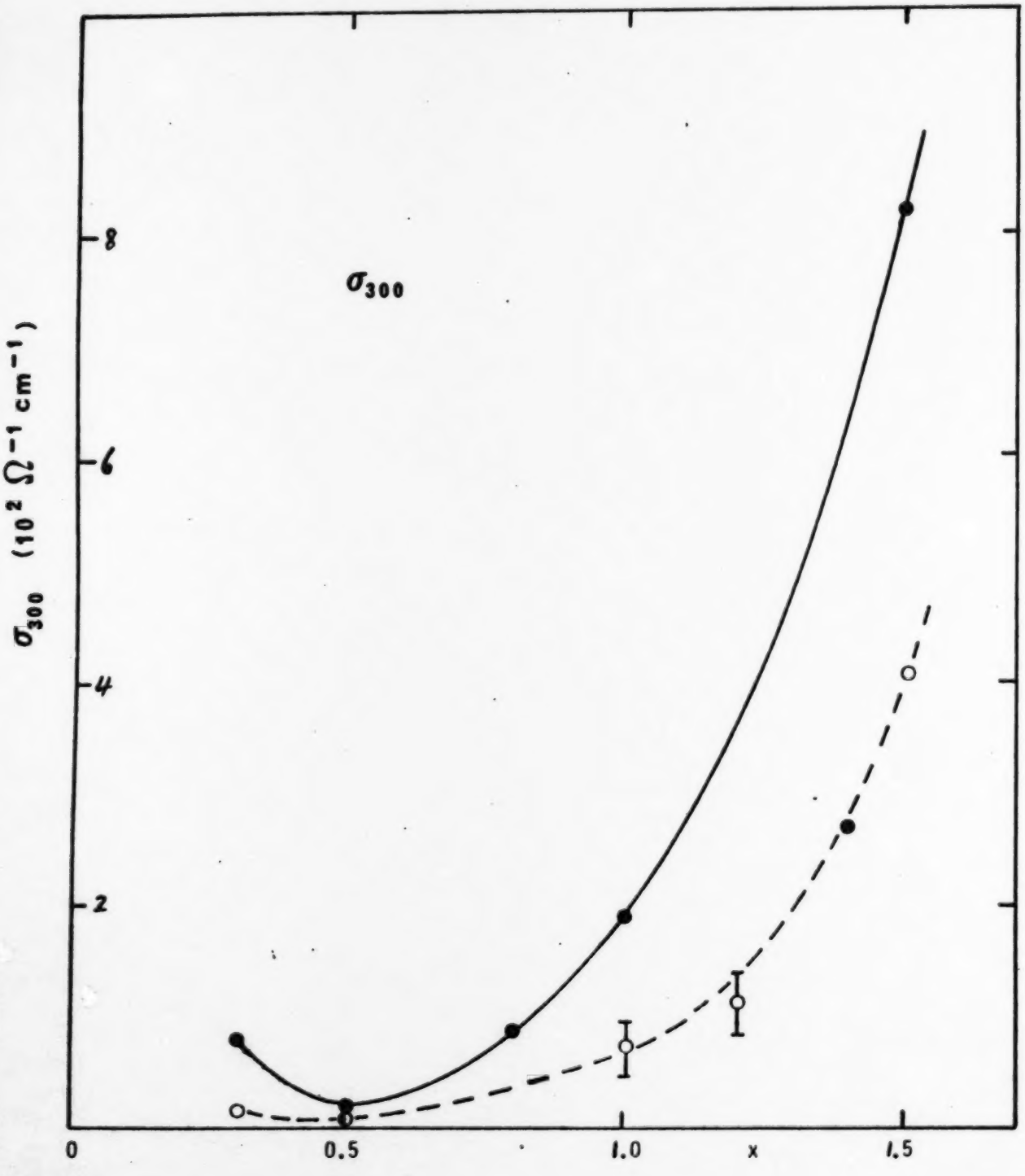


Figure 6 Variation of the conductivity with x in the rhombohedral phase.

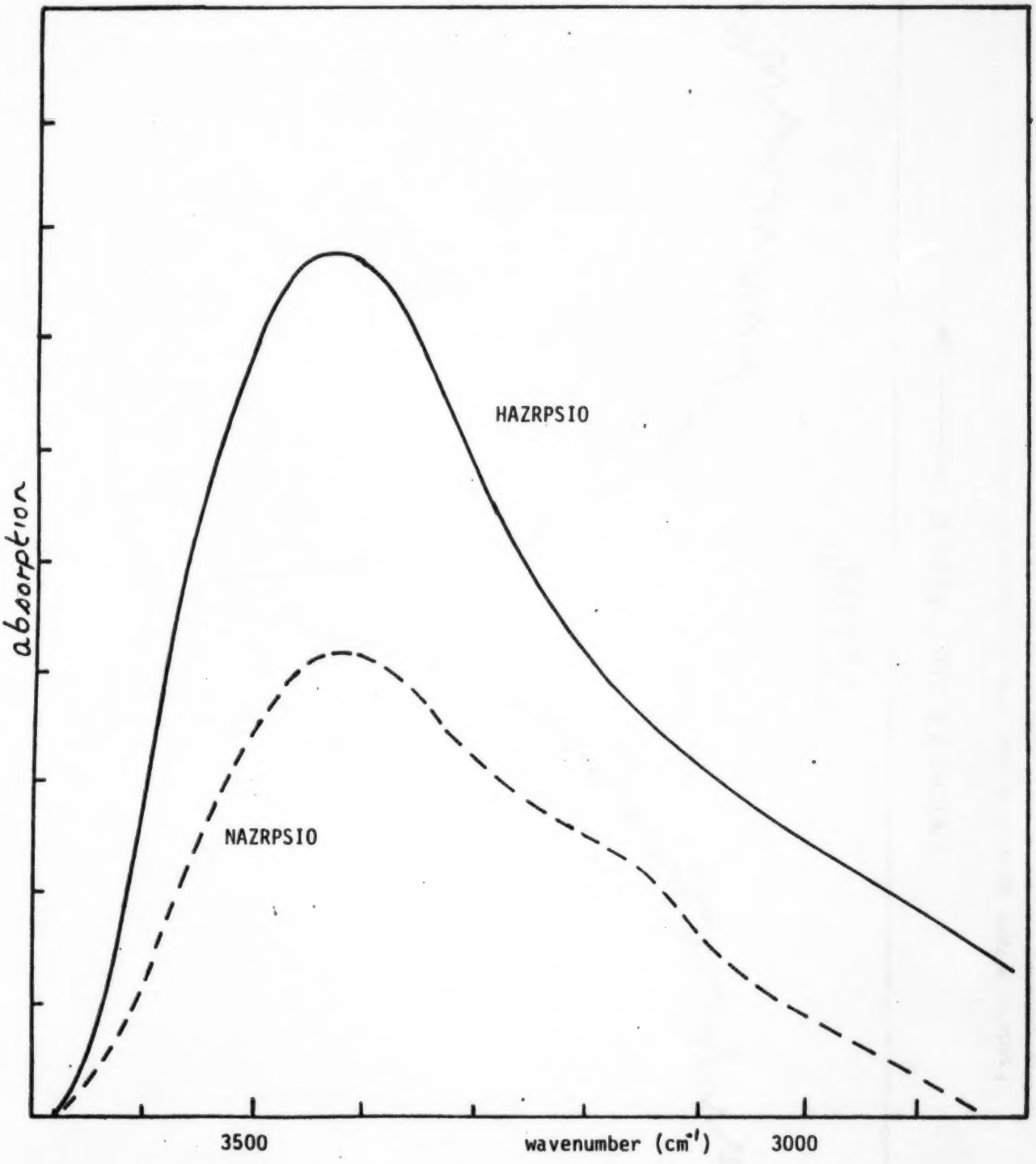


Figure 7 Infra-red spectra for NaZrPSiO and its proton analogue.

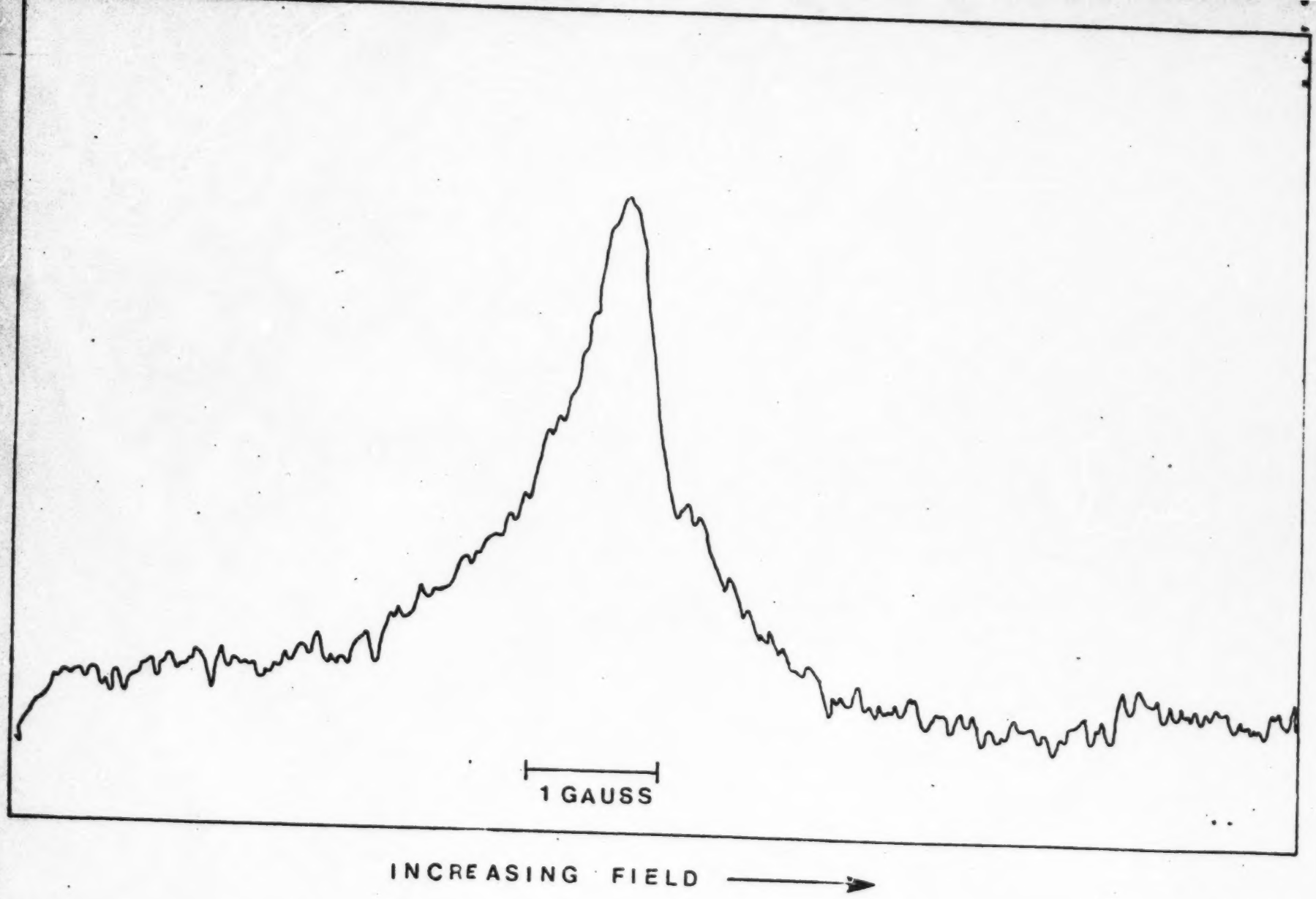


Figure 8 NMR spectrum for the exchange product.

...conductivity of the exchange product ... before and after

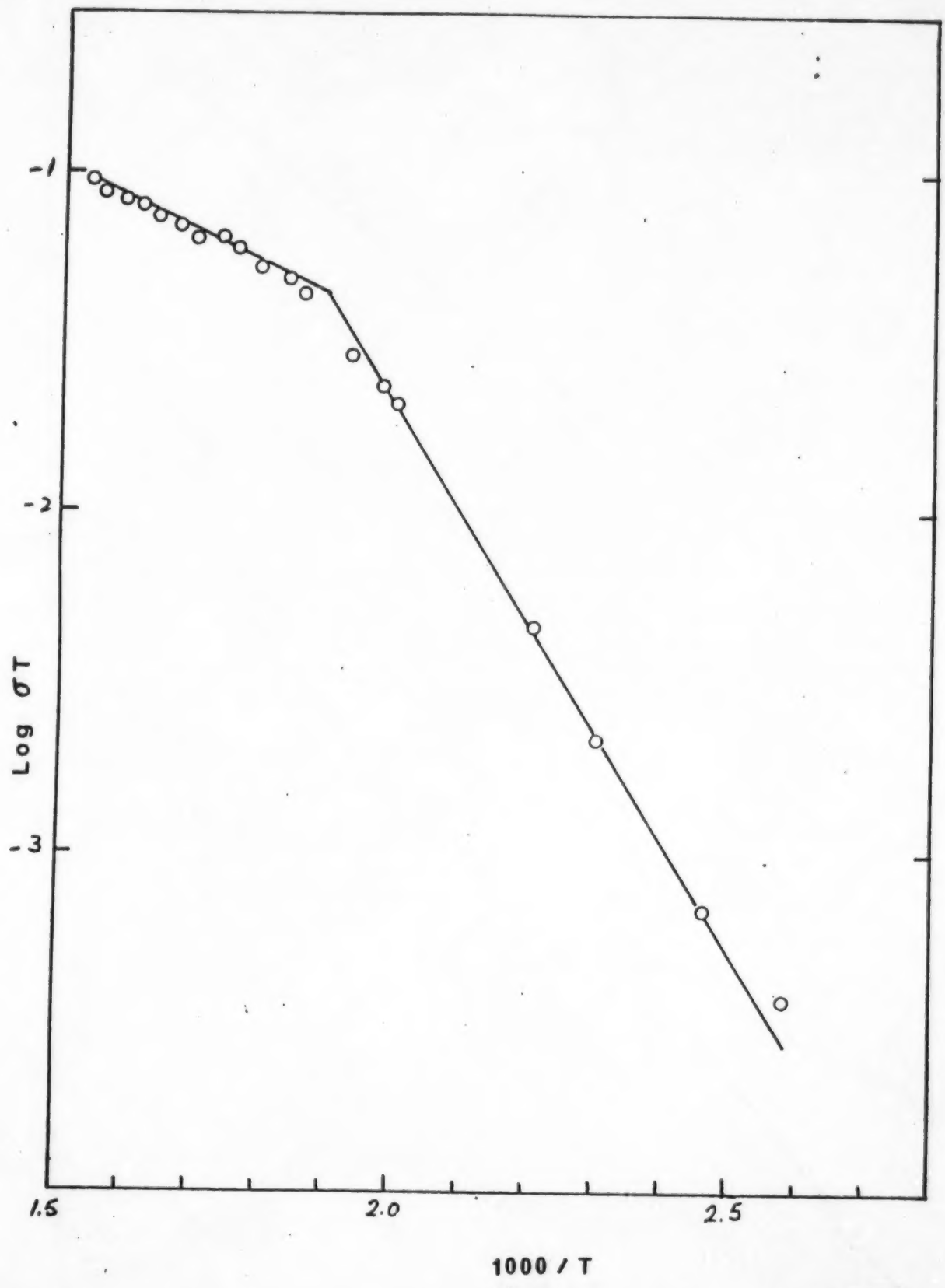
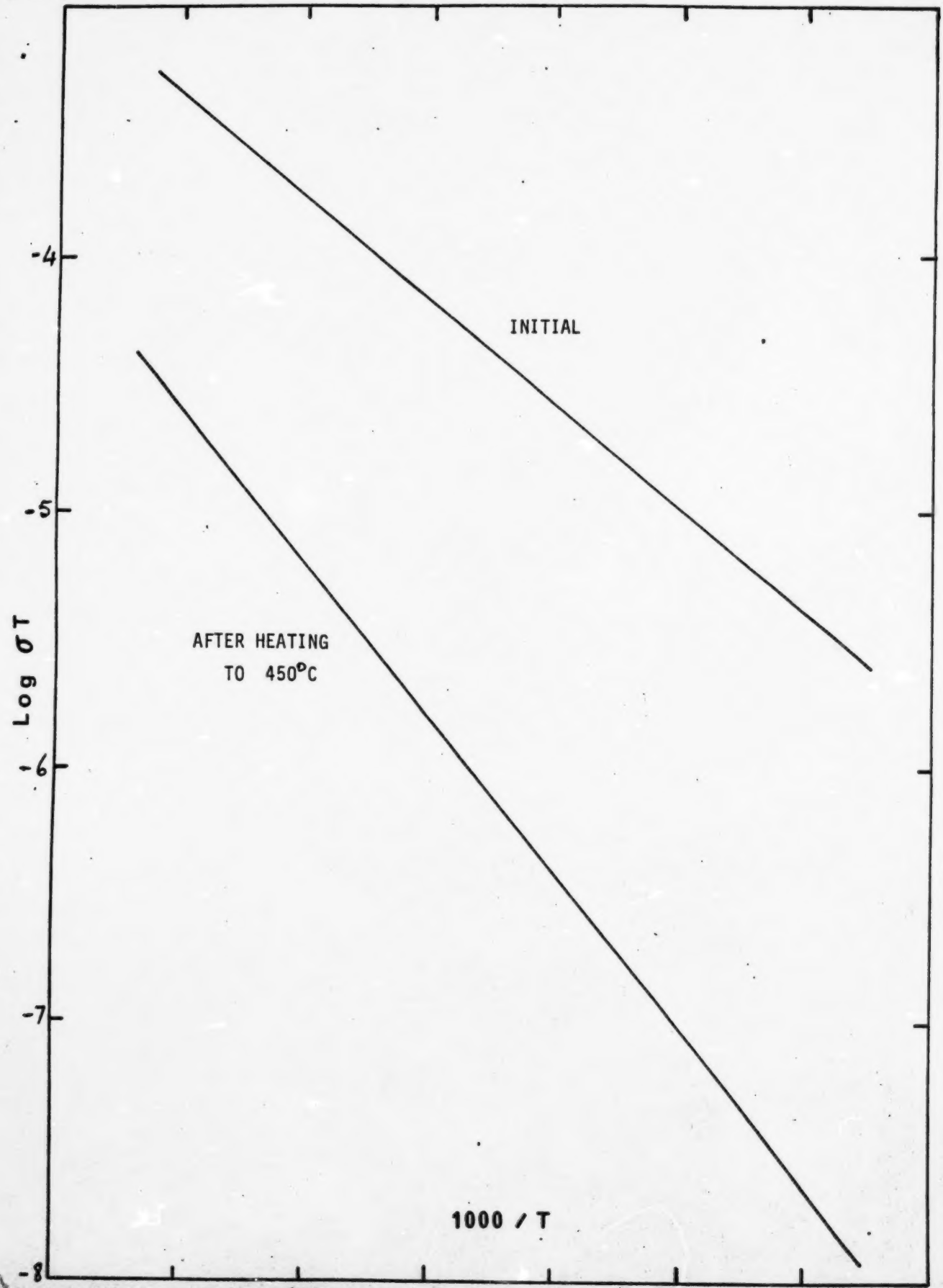


Figure 9 Conductivity for the exchange product (x=2) as a function of temperature.

Figure 10 Conductivity of the exchange product [illegible] and after heating to 450°C.



POOR

QUALITY

ORIGINAL